

CLAIMS

1. Thermoplastic elastomeric material comprising:

(a) from 10% by weight to 100% by weight of at least one styrene-based thermoplastic elastomer;

5 (b) from 0% by weight to 90% by weight of at least one thermoplastic  $\alpha$ -olefin homopolymer or copolymer different from (a);

the amount of (a) + (b) being 100;

(c) from 2 parts by weight to 90 parts by weight of a 10 vulcanized rubber in a subdivided form;

(d) from 0.01 parts by weight to 10 parts by weight of at least one coupling agent containing at least one ethylenic unsaturation;

15 the amounts of (c) and (d) being expressed with respect to 100 parts by weight of (a) + (b).

2. Thermoplastic elastomeric material comprising:

(a) from 20% by weight to 80% by weight of at least one styrene-based thermoplastic elastomer;

20 (b) from 20% by weight to 80% by weight of at least one thermoplastic  $\alpha$ -olefin homopolymer or copolymer different from (a);

the amount of (a) + (b) being 100.

3. Thermoplastic elastomeric material according to claim

1 or 2, wherein the vulcanized rubber in a subdivided form

25 (c) is present in an amount of from 5 parts by weight to 40 parts by weight with respect to 100 parts by weight of (a) + (b).

4. Thermoplastic elastomeric material according to any

one of the preceding claims, wherein the coupling agent is present in an amount of from 0.05 parts by weight to 5 parts by weight with respect to 100 parts by weight of (a) + (b).

5 5. Thermoplastic elastomeric material according to any one of the preceding claims, wherein the styrene-based thermoplastic elastomer (a) comprises at least two terminal poly(monovinylaromatic hydrocarbon) blocks and at least one internal poly(conjugated diene) block and/or poly(aliphatic 10  $\alpha$ -olefin) block.

6. Thermoplastic elastomeric material according to claim 5, wherein the styrene-based thermoplastic elastomer (a) is selected from block copolymers having the following formulae:  $A(BA)_m$ ,  $A(BA')_{m'}$ , or  $(AB)_nX$ , or  $(AB)_pX(A'B')_q$  or 15  $(AB)_rX(B'')_s$ , wherein each of A and A' independently represent a polymer block comprising a monovinylidene aromatic monomer; B, B' and B'' independently represent a polymer block comprising a conjugated diene monomer and/or an aliphatic  $\alpha$ -olefin monomer; X represents a 20 polyfunctional bridging moiety; n and r represent an integer not lower than 2; m and m' represents an integer  $\geq$  1; p, q and s represent an integer  $\geq$  1.

7. Thermoplastic elastomeric material according to claim 6, wherein the monovinylidene aromatic monomer of blocks A 25 and A' is selected from: styrene, alkyl-substituted styrenes, alkoxy-substituted styrenes, vinyl naphthalene, alkyl-substituted vinyl naphthalene, vinyl xylene, alkyl-substituted vinyl xylene, or mixtures thereof.

8. Thermoplastic elastomeric material according to claim 30 6 or 7, wherein the conjugated diene monomer of blocks B, B' and B'', is selected from conjugated dienes containing from 4 to 24 carbon atoms, such as 1,3-butadiene, isoprene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-phenyl-1,3-butadiene, 1,3-pentadiene, methylpentadiene, 3-35 ethyl-1,3-pentadiene, 2,4-hexadiene, 3,4-dimethyl-1,3-

hexadiene, 4,5-diethyl-1,3-octadiene, piperylene, or mixtures thereof.

9. Thermoplastic elastomeric material according to any one of claim 6 to 8, wherein the aliphatic  $\alpha$ -olefin monomer 5 is selected from ethylene, propylene, or mixtures thereof.

10. Thermoplastic elastomeric material according to any one of claims 6 to 9, wherein the polyfunctional bridging moiety comprises from 2 to 8 functional groups.

11. Thermoplastic elastomeric material according to any 10 one of claims 6 to 10, wherein the blocks copolymers are selectively hydrogenated.

12. Thermoplastic elastomeric material according to any one of claims 6 to 11, wherein the blocks A and A' have a weight average molecular weight in the range of from 3,000 15 g/mol to 125,000 g/mol.

13. Thermoplastic elastomeric material according to any one of claims 6 to 12, wherein the blocks B, B' and B'', have a weight average molecular weight in the range of from 10,000 g/mol to 300,000 g/mol.

20 14. Thermoplastic elastomeric material according to any one of claims 6 to 13, wherein the block copolymers have a total weight average molecular weight in the range of from 25,000 to 500,000.

25 15. Thermoplastic elastomeric material according to any one of claims 6 to 14, wherein the block copolymer has a triblock structure and may be of the linear or radial type, or any combination thereof.

30 16. Thermoplastic elastomeric material according to any one of claims 6 to 15, wherein the styrene-based thermoplastic elastomer (a) is selected from the following triblock copolymers: styrene-butadiene-styrene (S-B-S), styrene-isoprene-styrene (S-I-S), styrene-ethylene/butene-

styrene (S-EB-S), or mixtures thereof.

17. Thermoplastic elastomeric material according to any one of the preceding claims, wherein in the thermoplastic  $\alpha$ -olefin homopolymer or copolymer (b), different from (a),

5 the  $\alpha$ -olefin is an aliphatic or aromatic  $\alpha$ -olefin of formula  $\text{CH}_2=\text{CH}-\text{R}$ , wherein R represents a hydrogen atom; a linear or branched alkyl group containing from 1 to 12 carbon atoms; an aryl group having from 6 to 14 carbon atoms.

10 18. Thermoplastic elastomeric material according to claim

17, wherein the aliphatic  $\alpha$ -olefin is selected from: ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, or mixture thereof.

15 19. Thermoplastic elastomeric material according to claim 17, wherein the aromatic  $\alpha$ -olefin is selected from:

20 styrene,  $\alpha$ -methylstyrene, or mixtures thereof.

20. Thermoplastic elastomeric material according to any one of claims 17 to 19, wherein the thermoplastic  $\alpha$ -olefin homopolymer or copolymer (b) is selected from:

25 - propylene homopolymers or copolymer of propylene with ethylene and/or an  $\alpha$ -olefin having from 4 to 12 carbon atoms with an overall content of ethylene and/or  $\alpha$ -olefin lower than 10% by mole;

30 - ethylene homopolymers or copolymers of ethylene with at least one  $\alpha$ -olefin having from 4 to 12 carbon atoms and, optionally, at least one polyene;

- styrene polymers such as styrene homopolymers; copolymers of styrene with at least one  $\text{C}_1\text{-C}_4$  alkyl-styrene or with at least one natural or synthetic

elastomer such as polybutadiene, polyisoprene, butyl rubber, ethylene/propylene/diene copolymer (EPDM), ethylene/propylene copolymers (EPR), natural rubber, epichlorohydrin;

5 - copolymers of ethylene with at least one ethylenically unsaturated ester selected from: alkyl acrylates, alkyl methacrylates and vinyl carboxylate, wherein the alkyl group, linear or branched, has from 1 to 8 carbon atoms, while the carboxylate group, linear or branched, has from 2 to 8 carbon atoms; and wherein the ethylenically unsaturated ester is generally present in an amount of from 0.1% to 80% by weight with respect to the total weight of the copolymer.

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21. Thermoplastic elastomeric material according to claim 20, wherein the ethylene homopolymers or copolymers of ethylene with at least one  $\alpha$ -olefin having from 4 to 12 carbon atoms are selected from: low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), linear low density polyethylene (LLDPE), ultra-low density polyethylene (ULDPE), or mixtures thereof.

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22. Thermoplastic elastomeric material according to claim 20, wherein the copolymers of ethylene with at least one  $\alpha$ -olefin having from 4 to 12 carbon atoms and optionally at least one polyene are selected from:

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- elastomeric copolymers having the following monomer composition: 35 mol%-90 mol% of ethylene; 10 mol%-65 mol% of an aliphatic  $\alpha$ -olefin; 0 mol%-10 mol% of a polyene;
- copolymers having the following monomer composition: 75 mol%-97 mol% of ethylene; 3 mol%-25 mol% of an aliphatic  $\alpha$ -olefin; 0 mol%-5 mol% of a polyene.

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23. Thermoplastic elastomeric material according to claim 20, wherein the styrene polymers, different from (a), are:

syndiotactic polystyrene, atactic polystyrene, isotactic polystyrene, styrene-methylstyrene copolymer, styrene-isoprene copolymer or styrene-butadiene copolymer, styrene-ethylene/propylene (S-EP) or styrene-ethylene/butene (S-EB) 5 diblock copolymers; styrene-butadiene or styrene-isoprene branched copolymers; or mixtures thereof.

24. Thermoplastic material according to claim 20, wherein the copolymers of ethylene with at least one ethylenically unsaturated ester are selected from: ethylene/vinylacetate 10 copolymer (EVA), ethylene/ethylacrylate copolymer (EEA), ethylene/butylacrylate copolymer (EBA), or mixtures thereof.

25. Thermoplastic elastomeric material according to any one of the preceding claims, wherein the vulcanized rubber 15 in a subdivided form (c) has a particle size not higher than 10 mm.

26. Thermoplastic elastomeric material according to claim 25, wherein the vulcanized rubber in a subdivided form (c) has a particle size not higher than 5 mm.

20 27. Thermoplastic elastomeric material according to any one of claims 1 to 24, wherein the vulcanized rubber in a subdivided form (c) has a particle size not higher than 0.5 mm.

25 28. Thermoplastic elastomeric material according to claim 27, wherein the vulcanized rubber in a subdivided form (c) has a particle size not higher than 0.2 mm.

29. Thermoplastic elastomeric material according to claim 28, wherein the vulcanized rubber in a subdivided form (c) has a particle size not higher than 0.1 mm.

30 30. Thermoplastic elastomeric material according to any one of the preceding claims, wherein the vulcanized rubber in a subdivided form (c) comprises at least one crosslinked diene elastomeric polymer or copolymer of natural origin or

obtained by solution polymerization, emulsion polymerization or gas-phase polymerization of one or more conjugated diolefins, optionally blended with at least one comonomer selected from monovinylarenes and/or polar 5 comonomers in an amount of not more than 60% by weight.

31. Thermoplastic elastomeric material according to claim 30, wherein the crosslinked diene elastomeric polymer or copolymer is selected from: cis-1,4-polyisoprene, 3,4-polyisoprene, polybutadiene, optionally halogenated 10 isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, styrene/1,3-butadiene copolymers, styrene/isoprene/1,3-butadiene copolymers, styrene/1,3-butadiene/acrylonitrile copolymers, or mixtures thereof.

32. Thermoplastic elastomeric material according to any 15 one of the preceding claims, wherein the vulcanized rubber in a subdivided form (c) further comprises at least one crosslinked elastomeric polymer of one or more monoolefins with an olefinic comonomer or derivatives thereof.

33. Thermoplastic elastomeric material according to claim 20 32, wherein the crosslinked elastomeric polymer is selected from: ethylene/propylene copolymers (EPR) or ethylene/propylene/diene copolymers (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers, in particular chlorobutyl or bromobutyl rubbers; or mixtures thereof.

34. Thermoplastic elastomeric material according to any 25 one of the preceding claims, wherein the coupling agent containing at least one ethylenic unsaturation (d) is selected from: silane compounds containing at least one ethylenic unsaturation and at least one hydrolyzable group; 30 epoxides containing at least one ethylenic unsaturation; monocarboxylic acids or dicarboxylic acids containing at least one ethylenic unsaturation, or derivatives thereof; organic titanates, zirconates or aluminates containing at least one ethylenic unsaturation.

35. Thermoplastic elastomeric material according to claim 34, wherein the silane compounds are selected from:  $\gamma$ -methacryloxypropyltrimethoxysilane, methyltriethoxy-silane, methyltris(2-methoxyethoxy)silane, dimethyl-diethoxysilane, 5 vinyltris(2-methoxyethoxy)silane, vinyltrimethoxysilane, vinyltriethoxysilane, octyltri-ethoxysilane, isobutyltriethoxysilane, isobutyl-trimethoxysilane, or mixtures thereof.

10 36. Thermoplastic elastomeric material according to claim 34, wherein the epoxides are selected from: glycidyl acrylate, glycidyl methacrylate, monoglycidyl ester of itaconic acid, glycidyl ester of maleic acid, vinyl glycidyl ether, allyl glycidyl ether, or mixtures thereof.

15 37. Thermoplastic elastomeric material according to claim 34, wherein the monocarboxylic or dicarboxylic acids, or derivatives thereof, are selected from: maleic acid, maleic anhydride, fumaric acid, citraconic acid, itaconic acid, acrylic acid, methacrylic acid, and anhydrides or esters derived therefrom, or mixtures thereof.

20 38. Thermoplastic elastomeric material according to any one of the preceding claims further comprising at least one aromatic monocarboxylic or dicarboxylic acid or a derivative thereof (e) such as, an anhydride or an ester.

25 39. Thermoplastic elastomeric material according to claim 38, wherein the aromatic monocarboxylic or dicarboxylic acid or a derivative thereof is selected from: benzoic acid, phthalic acid, phthalic anhydride, trimellitic anhydride, di-2-ethylhexyl phthalate, di-isodecyl phthalate, tris-2-ethylhexyl trimellitate, or mixtures 30 thereof.

40. Thermoplastic elastomeric material according to claim 38 or 39, wherein the aromatic monocarboxylic or dicarboxylic acid or a derivatives thereof (e) is present in an amount of from 0 parts by weight to 10 parts by

weight with respect to 100 parts by weight of (a) + (b).

41. Thermoplastic elastomeric material according to claim 40, wherein the aromatic monocarboxylic or dicarboxylic acid or a derivative thereof (e) is present in an amount of 5 from 0.01 parts by weight to 5 parts by weight with respect to 100 parts by weight of (a) + (b).

42. Thermoplastic elastomeric material according to any one of the preceding claims further comprising at least one inorganic filler (f).

10 43. Thermoplastic elastomeric material according to claim 42, wherein the inorganic filler (f) are selected from: hydroxides, hydrated oxides, salts or hydrated salts of metals, in particular, of calcium, magnesium or aluminium, optionally in admixture with other inorganic fillers such 15 as silicates, carbon black, or mixtures thereof.

44. Thermoplastic elastomeric material according to claim 43, wherein the inorganic fillers are: magnesium hydroxide, aluminium hydroxide, aluminium oxide, aluminium trihydrate, magnesium carbonate hydrate, magnesium carbonate, calcium 20 carbonate hydrate, calcium carbonate, magnesium calcium carbonate hydrate, magnesium calcium carbonate, or mixture thereof.

45. Thermoplastic elastomeric material according to any one of claims 42 to 44, wherein the inorganic filler (f) is 25 present in an amount from 0 parts by weight to 200 parts by weight with respect to 100 parts by weight of (a) + (b).

46. Thermoplastic elastomeric material according to claim 45, wherein the inorganic filler (f) is present in an amount from 10 parts by weight to 50 parts by weight, with 30 respect to 100 parts by weight of (a) + (b).

47. Thermoplastic elastomeric material according to any one of the preceding claims further comprising at least one syndiotactic 1,2-polybutadiene (g).

48. Thermoplastic elastomeric material according to claim 47, wherein the syndiotactic 1,2-polybutadiene has an average molecular weight (number-average) of from 75,000 to 200,000.

5 49. Thermoplastic elastomeric material according to claim 47 or 48, wherein the 1,2-polybutadiene has a crystallinity degree of from 10% to 90%.

10 50. Thermoplastic elastomeric material according to any one of claims 47 to 49, wherein the syndiotactic 1,2-polybutadiene (g) is present in an amount of from 0 parts by weight to 300 parts by weight with respect to the 100 parts by weight of (a) + (b).

15 51. Thermoplastic elastomeric material according to claim 50, wherein the syndiotactic 1,2-polybutadiene (g) is present in an amount of from 5 parts by weight to 200 parts by weight, with respect to the 100 parts by weight of (a) + (b).

20 52. Thermoplastic elastomeric material according to any one of the preceding claims, further comprising a radical initiator (h).

25 53. Thermoplastic elastomeric material according to claim 52, wherein the radical initiator (h) is selected from organic peroxides such as t-butyl perbenzoate, dicumyl peroxide, benzoyl peroxide, di-t-butyl peroxide, or mixtures thereof.

54. Thermoplastic elastomeric material according to claim 52 or 53, wherein the radical initiator (h) is added in an amount of from 0 parts by weight to 5 parts by weight with respect to 100 parts by weight of (a) + (b).

30 55. Thermoplastic elastomeric material according to claim 54, wherein the radical initiator (h) is added in an amount of from 0.01 parts by weight to 2 parts by weight with respect to 100 parts by weight of (a) + (b).

56. Thermoplastic elastomeric material according to any one of the preceding claims, wherein the styrene-based thermoplastic elastomer (a) includes conjugated diene monomers and the thermoplastic elastomeric material is  
5 substantially devoid of a radical initiator (h).

57. Manufactured product obtained by molding a thermoplastic elastomeric material according to any one of the preceding claims.

10 58. Manufactured product comprising a thermoplastic elastomeric material according to any one of the preceding claims.

59. Manufactured product according to claim 57 or 58, said manufactured product being selected from: shoe soles, shoe foxing, shoe innersoles.

15 60. Manufactured product according to claim 57 or 58, said manufactured product being selected from: belts; flooring and footpaths; flooring tiles; mats; shock absorbers sheetings; sound barriers; membrane protections; carpet underlay; automotive bumpers; wheel arch liner; seals; o-rings; gaskets; watering systems; pipes or hoses materials; flower pots; building blocks; roofing materials; geomembranes.